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Ferroelectric-paraelectric phase transitions in P(VDF-TrFE) Langmuir–Blodgett films studied by optical second harmonic generation

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Abstract. Ferroelectric-paraelectric phase transitions are studied in Langmuir–Blodgett (LB) films of vinylidene fluoride with trifluoroethylene (P(VDF-TrFE)) by an electrode-free method of optical second harmonic generation (SHG). The temperature dependences of the SHG intensity are studied for the LB films of the thickness down to a monolayer and two peculiarities attributed to two different ferroelectric-paraelectric phase transitions are observed. A qualitative correlation between the temperature dependences of the static dielectric constant and the SHG intensity is underlined. The results are interpreted in terms of the spontaneous polarization induced lack of the initially centrosymmetric structure of the film which gives rise to an electro-dipole SHG.

The ferroelectrical properties of thin films of poly-vinylidene fluoride with copolymer trifluoroethylene P(VDF-TrFE) have been discussed intensively over the last years. The first PVDF films deposited by the Langmuir-Blodgett (LB) technique have been composed in the very late 1990's and recent results show that ultrathin LB films of this polymer behave as 2D ferroelectrics [1, 2]. The ferroelectric properties of these 2D structures were studied experimentally by traditional measurements of dielectric parameters. These methods require the deposition of a cap electrode on the top of the film consisting of only a few polymer monolayers, and thus a question always arises how undisturbed and reliable these measurements are.

Optical second harmonic generation (SHG) has been shown to be a simple, non-invasive and informative probe to study the properties of ultrathin (down to monolayers) films [3]. This advantage of SHG stems from its unique sensitivity to the breakdown of crystallographic symmetry. The inversion symmetry of bulky centrosymmerical material is broken at interfaces or, for example, in the presence of a DC electric field, and as a result the SHG in the bulk of a material is allowed in the electro-dipole approximation. By analogy with the external DC-electric field, a spontaneous polarization (SP) in ferroelectrics breaks down the inversion symmetry and produces strong dipole SHG which makes SHG a very sensitive probe of ferroelectricity and ferroelectric-paraelectric phase transitions. On the other hand, this is an electrode-free method which is non-invasive for ultrathin films.

Ferroelectric P(VDF-TrFE)(70:30 mol %) LB films were deposited onto a fused quartz substrate by Langmuir-Blodgett horizontal lift method. The thickness of a single monolayer of P(VDF-TrFE) LB film is approximately 0.5 nm. The films from 1 to 60 monolayers thick were studied. For the SHG measurements the output of a Q-switched YAG:Nd^{3+} laser at a wavelength of 1064-nm was used with a pulse duration of 15 ns and an intensity of 1 MW/cm^2 at an angle of incidence of 45°. The reflected SHG signal was selected

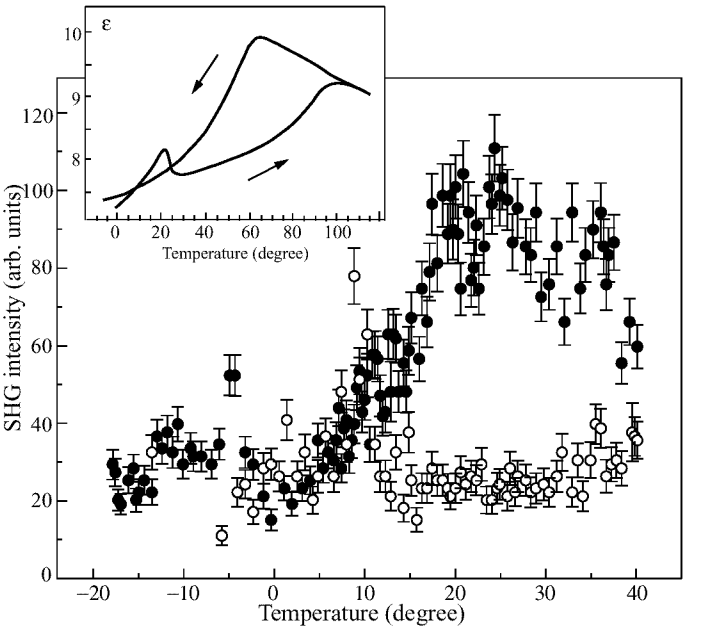

Fig. 1. The temperature dependence of the SHG intensity for a 60-monolayer-thick LB film. Filled and open symbols — the cooling and heating branches, respectively.

by bandpass filters and detected by a PMT and gated electronics. The p-in, p-plus-s-out (no analyzer) combination of polarization of the fundamental and second harmonic waves were measured in order to collect the depolarized and diffuse SHG radiation. The angular aperture of the detection system was approximately 10^{-1} sr. The temperature of the LB films placed into the optical cryostat was varied in the range from -30°C up to 120°C at a rate of 0.5 deg./min.

The main panel in the Figure shows the temperature dependence of the SHG intensity under the cooling and heating for a 60 monolayer thick P(VDF-TrFE) LB film. A clear hysteresis in the SHG intensity can be seen as the direction of temperature variation is changed. A sharp peak was observed under the heating of the film in the vicinity of 10–15°C, which can be related to a low-temperature ferroelectric-paraelectric phase transition observed previously by the static dielectric measurements. In [ ] this low-temperature phase transition was attributed to the ferroelectric properties of the surface layer of the P(VDF-TrFE) film. The second specific point in the SHG temperature dependences was observed at 30–40°C, which was determined as a maximum of the cooling branch of the SHG intensity temperature dependence. It corresponds probably to a 'bulk' ferroelectric-paraelectric phase transition [ ]. Similar dependences were observed for the films of various thickness. For a qualitative description of the temperature dependence of the SHG intensity in P(VDF-TrFE) LB films, we consider a nonlinear-optical model of the ferroelectric LB structure which involves the non-linear optical sources located at the film interfaces and in the bulk of the LB film. In the paraelectric phase and in the electro-dipole approximation, the SHG is determined by the surface contribution to the nonlinear polarization which originates from the discontinuity of the structure of the film in the normal direction. For the ferroelectric phase, additional electro-dipole contributions from both the surface and bulk should appear. Thus the SHG intensity, $I_{2\omega}(T)$, which is proportional to the square of

the nonlinear polarization, $\vec{P}_{2\omega}(T)$, $I_{2\omega}(T) \propto |\vec{P}_{2\omega}(T)|^2$, is determined by the vector sum of the following contributions:

$$\vec{P}_{2\omega}(T) = \hat{\chi}^{(2)s}_{2\omega}(T)\vec{E}_\omega\vec{E}_\omega + \hat{\chi}^{(3)s}_{2\omega}(T)\vec{E}_\omega\vec{E}_\omega\vec{P}^s_{sp}(T) + \hat{\chi}^{(2)b}_{2\omega}(T)\vec{E}_\omega\vec{E}_\omega + \hat{\chi}^{(3)b}_{2\omega}(T)\vec{E}_\omega\vec{E}_\omega\vec{P}^b_{sp}(T), \quad (1)$$

where the superscripts s and b are related to the surface and the bulk contributions, respectively, $\vec{E}_\omega$ is the electric field of the fundamental beam, $\vec{P}_{sp}(T)$ is the spontaneous polarization. Here the two types of the quadratic susceptibility tensors are described. First is the dipole second-order susceptibility tensor, which is always present at the surface of the film and which appears in the bulk of the film only in the ferroelectric state below the Curier temperature. This bulk term appears due to the modification of the crystalline structure of the film under the transition to the ferroelectric phase. Second, dipole third-order susceptibility tensors, which describe SP-induced contributions to $\vec{P}_{2\omega}(T)$.

As the static dielectric constant $\varepsilon(T)$ is a linear function of SP, the comparison of the temperature dependences of the SHG intensity and of the static dielectric constant can allow to determine the role of the SP-induced terms in the SHG. The inset in the Figure shows the $\varepsilon(T)$ dependence (after [ ]) measured for the 30 monolayer-thick P(VDF-TrFE) LB films. A clear qualitative correlation between these dependences shows that the SP-induced components to the nonlinear polarization play the main role in the temperature dependence of the SHG intensity. The differences in the values of temperature corresponding to the two types of the paraelectric-ferroelectric phase transitions and observed by the dielectric [ ] and nonlinear-optical measurements, can be caused, first, by the interference of the terms of the nonlinear polarization in (1), second, by the different temperature scanning rate in the SHG experiments. It should be mentioned that a strong temperature dependence and hysteresis of the SHG intensity can not be explained by the variations of optical refractive index and the corresponding changes in the Fresnel coefficients caused by the temperature-induced variations of the static dielectric constant.

In summary, optical SHG is used as an electrode-free method to study the 2D ferroelectric-paraelectric phase transitions in LB films of P(VDF-TrFE). Temperature dependence of the SP-induced SHG intensity reveals two peculiarities which can be attributed to a 2D ferroelectric phase transition in the interfacial layers of the LB films and a thickness independent (almost 2D) ferroelectric phase transition in the bulk of the LB films.

Acknowledgements

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References

[1] A. V. Bune, V. M. Fridkin, S. Ducharme, L. M. Blinov, S. P. Palto, A. V. Sorokin, S. G. Yudin and A. Zlatkin, *Nature* **391**, 874 (1998).

[2] S. Ducharme, A. Bune, L. M. Blinov, V. M. Fridkin, S. P. Palto, A. V. Sorokin and S. G. Yudin, *Phys. Rev. B* **57**, 25 (1998).

[3] J. F. McGilp, *Phys. Stat. Solidi A* **175**, 153 (1999).